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TRANSLATION

CERTAIN THEORETICAL PREREQUISITES ON
THE CONSTRUCTION OF METAL-
LIKE REFRACTORIES

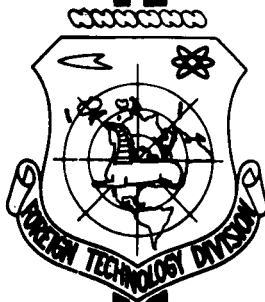
By

G. V. Samsonov and V. S. Meshpor

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Certain Theoretical Prerequisites on the Construction of Metal-
Like Refractories

by

G. V. Samsonov and V. S. Meshper

In this report are discussed the principal possibilities of preparing heat resistant alloys. It is pointed out in particular, that for effective utilization of metal-like compounds in role of refractory materials is necessary to obtain compounds possessing not too high forces of interatomic reaction and at the same time a very great mass of the structural complex, which will increase the ability of these substances toward relaxation of elastic stresses, reduce their brittleness and increase resistance to thermal impact.

The continuously growing requirements set forth for refractories for all their parameters - strength at high temperatures, resistance against thermal impact, corrosion and erosion stability, prompt the necessity of thoroughly examining solid high melting substances, which appear to, in particular, metal like carbides, nitrides, borides and silicides[1].

The clearest basic principles of creating heat resistant fusions have been formulated by academician A.A. Bochvar[2]. It classifies possible methods of increasing the strength of metals and alloys at high temperatures into the following four groups:

1) method of distorting the crystalline lattice at mechanical deformation at low temperatures; 2) by forming solid solutions; 3) during the formation of a highly dispersion mixture of phases; 4) upon the introduction into the alloy of components, forming a more solid phase in form of skeleton between the grains of the basic metal and alloy.

The first two of these methods are connected with reinforcing by distorting the crystalline lattice or by increasing the forces of interatomic reaction in solid so-

lutions and the two remaining ones - with the difficulty of sliding by heterogenization of structure, whereby the most effective appears to be the formation of skeleton or screen of heat resistant phase of the alloy.

In metal fusions (alloys) the strengthening effect of lattice distortion with a rise in temperature weakens as result of rise in the mobility of atoms and development of diffusion processes, leading to the removal of the stressed state or to ordering the structure of solid solutions.

In case of skeletal nature of formation of a strengthening phase there is a reduction in strength upon heating which is due to the rise in solubility of this phase in basic alloy.

From the view point of these heat resistance principles are highly interesting metal-like compounds, a considerable part of which is either constructed by the type of introduction phases, or contain structural elements, distorting and reinforcing the crystalline lattice.

Carbides of a series of transient metals represent typical phases of introduction, i.e. lattices of metallic atoms, in the pores of which are introduced metalloid-carbon atoms (fig.1), with the adherence to metal atom and metalloid radii $R_X: R_{Me} \leq 0.59$.

An analogous structure is also possessed by many nitrides. It is apparent, that the introduction of carbon atoms into the pores of metallic cells as well as the formation of carbon atom chains (for example, in chromium carbides) leads to the hardening of crystalline lattice and hampering of displacement deformation.

Borides of transient metals according to Kiesling [3] are characterized by strong bonds between the boron atoms, whereby these bonds become strengthened with an increase in boron content in boride phases. And so, in Me_4B and Me_2 type compounds the boron atoms are isolated from each other, in MeB compounds are formed zig-zag like single chains, in Me_3B_4 - binary chains, in MeB_2 (fig.2) screens and, finally, in MeB_4 , MeB_6 and MeB_{12} compounds - a three dimensional lattice, in the pores of which are situated metal atoms. Parallel with the complication of structural elements

consisting of boron atoms, bound by strong covalent bonds, there is a rise in the strengthening of the lattice.

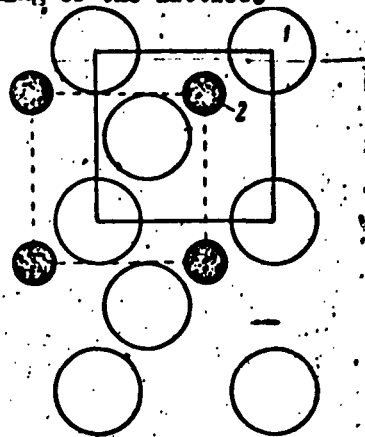


Fig.1. Introduction phases with dense cubical packing of metallic atoms: 1-atoms of metal; 2-carbon or nitrogen atoms.

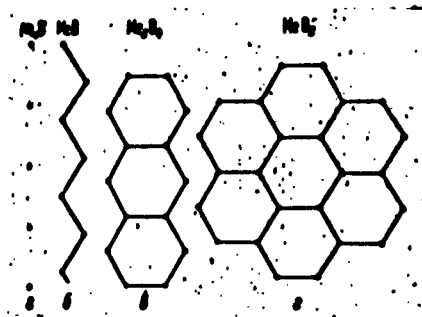


Fig.2. Structural elements of boron atoms in lattices of borides: a-isolated boron atoms (Me_2B borides); b-chains of boron atoms (MeB); c- doubled boron atom chains (Me_3B_4); d) screens (MeB_2 borides).

Silicides of high melting transient metals formed no longer by the principle of introduction but by the principle of replacing metallic atoms of silicon [4] .

Formation of graphite-like flat layer of silicon atoms in structures of many silicides (fig.3) leads to their low resistance to deformation, low hardness, low melting points etc, as compared with carbides, borides and nitrides. In this way, silicon atoms either weakly strengthen or even somewhat weaken the lattices of basic metals. This weakening appears, e.g. with a reduction in melting point of the metals during the formation of silicides by 1.2 to 1.8 times; but the simultaneous rise in hardness results in the formation of quite strong bonds between the atoms of metal and silicon in their layers.

The presence of introduced atoms, structural elements from metalloid atoms etc, in carbides, nitrides, borides and silicides should hamper the development of sliding processes, whereby it is considerably more effective, than, for example, the formation of solid solutions or presence of lattice distortions in pure metals, where, as was pointed out, these stressed states can be relatively easily liquidated by diffu-

sion processes.

In metal-like compounds heterogeneities in the scale of the elementary nucleus can be reduced by raising the temperature but only to such a degree, in which the bonds between metal atoms and metalloids weaken (i.e. the stressed state in these phases is not removed all the way to melting).

See attached page 4a for Figure 3

It is known, that the maximum value of critical shearing stress, determining the resistance of the crystalline body to plastic

deformation and to a known extent also its hardness, constitutes theoretically about 0.1 of the displacement modulus, and practically - not more than hundreds and thousands of fractions. The hardness/shear

Fig. 3. Structural elements from silicon atoms in silicide lattices: a - graphite-like trickles of silicon atoms; b - ditto, but centered by metal atoms; c - diamond like corrugated silicon atom screens.

coefficient ratio, for this reason can serve as a measure of strengthening the metal or alloy under given conditions¹.

For example, according to Ya. S. Umanskiy for low melting alloys (capable of weakening in the process of plastic deformation at room temperature) the hardness ratio of maximum strengthened alloy to shear coefficient of basic metal varies between 0.52 to 0.53, and for alloys with melting points of over 1300°C it reaches up to 0.082 - 0.088.

Analogous $H_M: G$ ratios, i.e. where H_M - microhardness in kg/mm^2 , have been calculated by us for a series of carbides and borides [6] and are listed in table 1

The $H_M: G$ ratio, i.e. the degree of strengthening, drops with a decrease in inter-

1. B. M. Rovinskiy [5] on the basis of analyzing experimental data showed, that hardness of annealed metal depends linearly upon the square of the elasticity modulus, and consequently, also the shear coefficient. Deviation from this dependence should, in this way, serve as a measure of nonequilibrium in the state of metallic lattice.

FIGURE 3

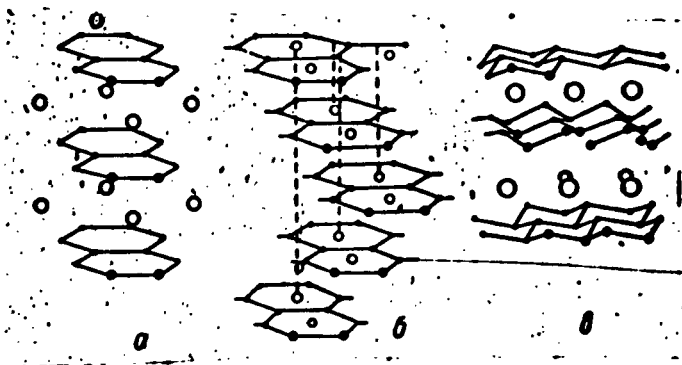


Figure 3

atomic reaction forces from 0.263 for TiC to 0.079 for WC.

Table 1. Comparison of shear modulus and microhardness of metal-like compounds

1) Compound	2) $H_M:G$	3) Compound	4) $H_M:G$
	Carbide	Boride	Carbide
	2	3	4
TiC	0.263	NbC	0.184
TiB ₂	—	TaC	—
TiN	—	CrB ₂	0.243
ZrC	0.236	MoC	0.074
ZrB ₂	—	WC	0.180
VC	0.220	WC	0.079

The latter value is close to such for ordinary high melting metals and alloys, and for remaining metal-like phases by 2-4 times higher, than for high melting, maximum strengthened metals, which indicates a considerably greater strengthening potential of these phases as compared with metals, which, in spite of the difficult sliding as result of atom introduction effect, is explained, (and this appears to be most important) by greater forces of interatomic bond of these compounds. This is evident by the greater importance of microhardness numbers of metal-like phases (table 2), which are on an average by an order greater, than for corresponding metals, and high melting points.

Calculation of energy of crystalline lattices for a series of metal-like compounds by the use of the method, introduced by E.S. Sarkisov [7] with consideration of participation in the bond, in addition to s-, also of d-electrons of the metal [6] shows (table 2), that these values are of the order of magnitude of 10^3 kcal/mol, which explains the high chemical strength of these phases, their greater hardness and high degree of strengthening, expressed by the $H_M:G$ ratio.

It can be seen that maximum bond energy is possessed by carbides and nitrides and lower one - by borides.

The hardness of metal-like compounds does not follow parallel with the change in bond energy, and depends substantially upon the structure. For example, if the energy of interatomic reaction in borides is close to such in carbides (ratio $U_{MB_2} : U_{MC} > 0.8$), then the greater difficulty in shear deformation, caused by the

strengthening effect of structural boron atom elements in boride lattices, leads to the point, that they are harder than the carbides. If the energy of boride lattices is considerably lower than such for carbides, then the structural factor is in no position to compensate the reduction in interatomic bond and the weakening of the lattice. In this case the hardness of borides is lower than the hardness of carbides. In nitrides the hardness, as a rule, is lower, than in carbides and borides.

The high energy of interatomic reaction in metal-like compounds promotes the strengthening state of these phases to very high temperatures, close to melting points.

A characteristic feature of metal-like compounds appears to be brittleness and low resistance against thermal impact, which sharply reduces their effective strength and limits their application in role of structural materials.

In report [8,9] we have shown, that very strong interatomic bonds lead to considerable reduction in the ability, of crystalline lattices of metal-like phases, toward relaxation of elastic stresses during mechanical stressing of objects from these substances. This causes localization of stresses on microdefects in the zone of stressing and the formation of cracking sources. Further concentration of stresses on these sources leads to their progressive development and toward rapid destruction of metal-like bodies, bearing the nature of "brittle fracture".

In the role of measure of ability of solid compounds toward the relaxation of elastic stresses can be considered mean square displacements of centers of structural complexes in the lattices of these compounds [9], calculated by elastic constants.

Heat resistance of brittle solid bodies should to a considerable degree depend upon the change in amplitude of thermal oscillations of atoms with temperature.

In table 3 are given RMS displacements of structural complexes for certain compounds, calculated from experimental values of linear expansion coefficients of poreless samples at two temperatures, hence it is evident, heat resistance of carbide (molybdenum carbide) should, at other conditions being equal, exceed the heat resistance of other carbides, listed in the table.

Table 2. Energy of lattices, microhardness, characteristic temperature, as well as melting point of metal-like compounds

(1) Phase	(2) H_m	(3) K_T	(4) θ_K	(5) T_m	(6) Phase	(7) U	(8) H_m	(9) K_T	(10) θ_K	(11) Phase	(12) U	(13) K_T	(14) θ_K	(15) T_m
	$\frac{\text{kcal}}{\text{mol}}$	$\frac{\text{mm}^2}{\text{mm}^2}$	$^\circ\text{K}$	$^\circ\text{K}$	$\frac{\text{kcal}}{\text{mol}}$	$\frac{\text{kcal}}{\text{mol}}$	$\frac{\text{kcal}}{\text{mol}}$	$\frac{\text{mm}^2}{\text{mm}^2}$	$^\circ\text{K}$	$\frac{\text{kcal}}{\text{mol}}$	$\frac{\text{kcal}}{\text{mol}}$	$\frac{\text{mm}^2}{\text{mm}^2}$	$^\circ\text{K}$	$^\circ\text{K}$
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
TiC	3880	2988	741	3140	TiB ₂	3280	3370	615	2900	TiN	3900	2160	617	2850
ZrC	3470	2925	490	3530	ZrB ₂	2640	2252	481	3040	ZrN	3540	1988	—	2980
HfC	2800	2800	—	3890	HfB ₂	—	—	—	3250	HfN	2840	—	—	3310
VC	3900	2094	531	2830	VB ₂	2880	2077	—	2400	VN	3820	—	—	2050
NbC	3216	1981	470	3500	NbB ₂	3060	2200	—	3000	NbN	3660	—	—	2050
Nb ₂ C	2570	2123	—	—	—	—	—	—	—	—	—	—	—	—
TaC	2770	1599	318	3880	TaB ₂	2940	2500	—	3100	TaN	3320	3236	—	3360
Ta ₂ C	2300	1714	—	—	—	—	—	—	—	—	—	—	—	—
Mo ₂ C	2280	1499	464	—	Mo ₂ B	2620	1790	—	2100	Mo ₂ N	2670	—	—	pass- reacts
WC	2760	1780	453	2030 (pass.)	—	—	—	—	—	—	—	—	—	—
W ₂ C	2000	3000	299	—	W ₂ B	2470	2350	—	2860	W ₂ N	—	—	—	pass- reacts

Table 3. Change in RMS displacement of structural complexes of metal-like phases with temperature

ϕ_{12}	$(\sqrt{u^2})_1$ nm 20°C at	$(\sqrt{u^2})_2$ nm 1000°C at	$(\sqrt{u^2})_2 - (\sqrt{u^2})_1$	$\Delta u/\Delta T \times 10^6$
TiC	0.067	0.187	0.120	7.1
ZrC	0.074	0.166	0.092	9.4
MoC	0.055	0.098	0.043	4.5
WC	0.058	0.134	0.076	7.7
W ₂ C	0.062	0.147	0.085	8.9
TiB ₂	0.073	0.178	0.105	10.2
ZrB ₂	0.072	0.143	0.071	7.2
VB ₂	0.083	0.158	0.075	7.5
TaB ₂	0.079	0.150	0.071	7.2

Zirconium boride, apparently, should be much more heat resistant, than carbide, and this explains the fact, why the latter found no great application in refractory materials, while boride is being widely used for the very same purpose in "borolite" type compounds. Titanium boride should have a much lower heat resistance, and, as is known, it has no great application in the role of refractory material. By the intensity of the originating thermal stresses titanium carbide and borides Zr, V and Nb are most likely close to each other.

A change in oscillations amplitude of structural complexes with temperature is connected with their mass and force of interatomic reaction, decreasing with its increase. But the very force of interatomic reaction generally decreases with a rise in mass of the Me-X complex, i.e. there is a rise in the shielding of unfilled d-shell of the metal, building special properties of metal-like compounds.

It can be expected, that the least change in RMS displacements of structural complexes in relation to temperature, will characterize Nb, Ta, Cr and Mo compounds having sufficiently high atomic mass and not too strong screening of the d-shell, which is evident from comparing the energies of crystalline lattices of metal-like compounds.

An important quality of heat resistant material appears to be the coefficient of linear expansion and the nature of its change with temperature. The greater value of the latter, apparently, offers a greater probability for the origination in

the body of thermal stresses of microscopic nature and irregular distribution of same due to the presence of defects in the body. It should be mentioned however, that directly from the value of thermal linear expansion coefficient it is impossible to determine the magnitude of thermal stresses, originating in the crystalline lattice of the body.

In table 4 are given values of linear expansion coefficients of a number of metal-like compounds at 200 °C and at 1000 °C-change in percentages, and in fig. 4-the temperature dependence the dependence of the linear expansion coefficient.

It can be expected from these data that carbide objects should be more stable against thermal impact, than boride objects, in spite of the fact that the value of thermal of thermal stresses, as it appears in fig. 4

See page 9a for Figure 4

Fig. 4. Temperature dependence of thermal expansion coefficients of metal-like compounds.

ZrC and Ti₂C. In practice boronitride objects (ZrB₂ with bundle (10,11)) are more heat resistant than from TiC and even ZrC, but objects made of TiC base alloys do much exceed the heat resistance of TiB₂ -base alloys. The high heat resistance of chromium boride is known [12]

That is why the thermal coefficient of linear expansion appears to be a less reliable characteristics for evaluating the intensity of thermal stresses in a crystalline lattice than the RMS displacement (shear) values of structural complexes.

With the increase in porosity of samples the degree of rise in thermal coefficient of linear expansion with temperature increases. We have here, naturally, an increase in irregularity in deformation distribution over the sample, on account of which there could appear additional thermal stresses of macroscopic nature, although the intensity of stresses, acting in the volume of the elementary nucleus, remains unchanged (or practically unchanged) with the change in density of the sample. From this viewpoint when manufacturing boundless refractory objects preference should be given to poreless items, especially since there is a substantial rise in resistance to gaseous

FIGURE 4

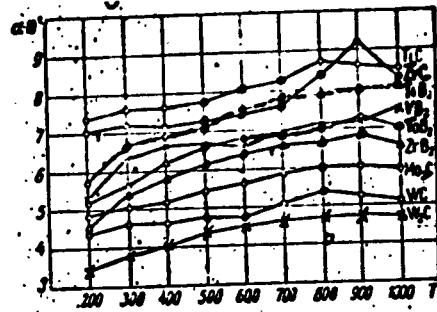


Figure 4

corrosion and in the strength of objects. But an increase in the density of the object together with a certain reduction in thermal stresses should considerably reduce the ability of the object in scattering the originating stresses on macroscopic scale, which for metal-like compounds is of first line importance because of their insignificantly low plasticity resources.

Table 4. Dependence of thermal expansion coefficient of metal-like compounds upon temperature

1) Phase	2) Thermal expansion coeff. $\alpha_s \cdot 10^6$	3) Rise in thermal coeff. in range of 200-1000°	4) Increase in %
	at 200°	at 300°	
	1	2	3
TiC	7.3 6.94	8.26 8.4	0.96 1.46
MoC ₂	4.8 4.45	5.93 5.1	1.13 0.65
TiB ₂	3.4 5.65	4.72 8.2	1.32 2.55
TaB ₂	4.45 5.27 5.1	6.64 7.5 7.0	2.19 2.23 1.9
			13.2 21.1 23.6 14.6 39.0 45.2 49.3 42.4 37.4

The lower the intensity of thermal stresses in the crystalline lattice of the substance and the greater the dispersibility of the lattice with respect to elastic stresses, the denser should be the object, made from this substance.

Important qualities of metal-like compounds as refractory materials appear to be their melting points. These compounds are very high melting, whereby their melting point, as is evident from table 2, rises with the increase in the number of the metallic

components in the group, just as it is for pure metals, which points toward the greater role in the heat resistance of these compounds of metal-metal bonds and mass of structural complexes.

Taking into consideration the above described qualities of metal-like compounds, it should be concluded, that for effective utilization of same in role of heat resistant materials it is necessary to obtain compounds, possessing not too high interatomic reaction forces and simultaneously not very high mass of structural complex, which will increase the ability of these substances toward relaxation of elastic

stresses, reduce their brittleness and raise the resistance to thermal impact, i.e. will allow a more thorough utilization of the high potential strength of metal-like compounds.

For the realization of other principal possibilities of preparing refractory alloys- by separating finely dispersed structural component or formation of a honeycomb (skeletal) structure- it is necessary to make a thorough investigation of phase diagrams of corresponding systems of metal-like compounds, especially with small change in solubility in solid state with temperature, i.e. with sloping curve of solubility boundary. In the role of an example it is possible to bring forth alloys of the $ZrB_2-(Ti, Cr)B_2$ profilr, investigated by K.I. Portniy and one of the authors [13].

The application of this principle to a greater number of objects will allow, evidently, to reach the obtainment of alloys, capable of withstanding considerable long lasting loads at high temperatures. We speak here of alloys without metallic bundles, which is highly important in this respect, that the bundle adds ordinarily, in addition to a rise in strength, a whole series of negative factor, such, as increased oxidizability, creepability, low natural heat resistance.

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